Superconductivity and fast proton transport in nanoconfined water

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ABSTRACT

A real-space molecular-orbital density-wave description of Cooper pairing in conjunction with the dynamic Jahn–Teller mechanism for high-T_c superconductivity predicts that electron-doped water confined to the nanoscale environment of a carbon nanotube or biological macromolecule should superconduct below and exhibit fast proton transport above the transition temperature, $T_c \cong 230$ K (-43 °C).

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1. Introduction

A major goal of superconductor research and development is the discovery of useful substances that superconduct at the highest possible transition or critical temperatures, T_c. The Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity [1], which ascribes the onset of the superconducting state at the transition temperature T_c to electrons attractively paired via virtual phonons, has been eminently successful in explaining conventional, relatively low-T_c superconductors. However, BCS theory in its simplest form has failed to explain the origin of the high-T_c superconductivity of doped cuprates [2]. Coupled with the dynamic Jahn–Teller (DJT) effect [3] and density-functional calculations for clusters representing the local molecular environments in superconducting materials [4], a *real-space molecular-orbital* description of electronic wave functions which are precursors of the superconducting state in high- and low-dimensional metals was proposed and applied to a variety of superconductors [5]. According to this scenario, superconductivity is possible only if the normal chemical bonding system in the material or parts thereof permits the construction of vibronically-coupled degenerate or nearly-degenerate ("pseudo" Jahn–Teller effect) molecular-orbital wave functions at the Fermi energy (E_F) which, for at least one space direction, are not topologically intersected by plane or conical nodal surfaces.

This translates to the requirement of spatially delocalized molecular orbitals at E_F that are bonding along "channels" of opposite phase, Ψ_+ and Ψ_- which are a *coordinate-space density-wave* basis for the *Cooper-pair wavefunction*,

$$\Phi(\mathbf{r}) = <\Psi_+(\mathbf{r} + \mathbf{d}/2)\Psi_-(\mathbf{r} - \mathbf{d}/2)>, \qquad (1)$$

where $\mathbf{r}$ is the pair spatial vector and d is the distance between the Ψ_+ and Ψ_- "channels", beyond which the electron–electron repulsion at E_F is largely screened out by the intervening ion cores (see Figs. 2, 4, and 5) [5]. The theory was applied to conventional metallic and organic superconductors [5,6], high-T_c cuprates [6], and superconducting potassium-doped carbon fullerene [7], yielding T_c-values, coherence lengths, isotope shifts, Debye frequencies, and thermodynamic critical magnetic fields in good agreement with experiments. Major findings include the association of cuprate high-T_c superconductivity with DJT vibronically-coupled, mainly oxygen orbitals at E_F, the prediction of 230 K (-43 °C) as the upper limit of T_c, and reduction of the theory to conventional BCS theory in the limit of harmonic vibronic (electron–phonon) coupling [5,6]. In the present paper, we propose that *supercooled, nanoscopically confined, electron-doped* water should superconduct up to the highest predicted $T_c \cong 230$ K due to DJT-induced terahertz (THz) vibrations of the component water nanoclusters coupled with their degenerate, mainly oxygen molecular orbitals at E_F. *Above* $T_c \cong 230$ K, nanoconfined water should exhibit high proton conductivity.

2. Review of the theory applied to high-T_c cuprates and fullerenes

Common to all the high-Tc cuprates is the approximately square-planar CuO_4 coordination complex forming the CuO_2 layers. Key to understanding both the parent insulating and superconducting phases of the cuprates is the strong covalency between the copper 3d atomic orbitals and the oxygen 2p valence orbitals, as compared with transition metals and oxygen. As a result, the relative ordering and characters of the Cu(d)-O(p) σ and π molecular-orbital levels in a CuO_4 coordination complex, determined from density-functional theory and shown in Fig. 1(b)
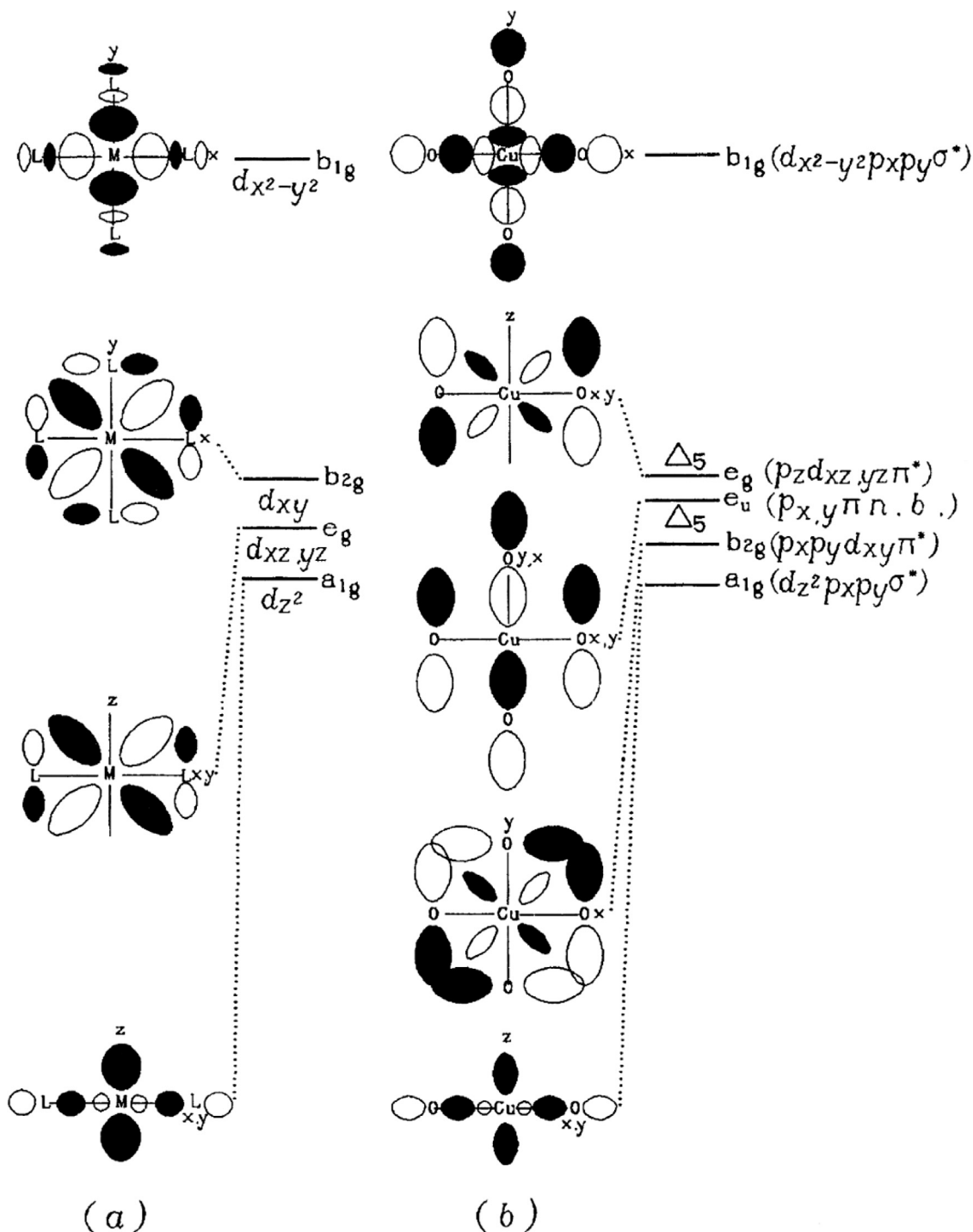
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Fig. 1. (a) Ligand-field electron states of a typical square-planar transition-metal complex, ML$_4$. (b) Molecular-orbitals of a square-planar CuO$_4$ cluster.

are significantly different from those of the ligand-field levels for a typical ionic transition-metal complex ML$_4$ shown in Fig. 1(a). This is due to the strong Cu(d$_{xz,yz}\pi^*$)-O(p$_z\pi$) covalent *antibonding* hybridization. It may be noted that some previous theories of high-T$_c$ superconductivity have assumed that the ordering of electron states in the doped CuO$_4$ complexes of the CuO$_2$ layers are the same as the ML$_4$ ligand-field levels of Fig. 1(a). That is simply incorrect. Occupancy of the strongly localized σ^*-antibonding b$_{1g}$ Cu(d$_{x^2-y^2}$)-O(p$_{x,y}$) orbital shown schematically in Fig. 1(b) is associated with the non-superconducting state of *undoped* cuprates. *Hole doping* leads to partial occupancy of the doubly degenerate e$_g$ O(p$_z$)-Cu(d$_{xz,yz}$) π^*-*antibonding* molecular orbital shown schemati-

cally in Fig. 1(b) and in the density-functional e$_g$(xz) wavefunction contour map of Fig. 2. Note the predominant O(p$_z\pi$) character. These coordinate-space e$_g$ orbitals correspond to the **k**-space *flat-band 4 and Van Hove singularity* at E$_F$ above the mainly oxygen-like valence band shown in the reproduced Fig 3(a) [8]. The real-space e$_g$(xz) molecular-orbital wavefunction contour map of Fig. 2 is very similar topologically to the charge-density map shown in Fig. 3(b) for this flat-band Van Hove singularity [8]. The key consequence of this strong O(p$_z$)-Cu(d$_{xz,yz}$) π^*-antibonding hybridization at E$_F$ for optimally doped high-T$_c$ cuprates (not pointed out previously in publications by other authors) is the promotion of substantial O(p$_z\pi$)-O(p$_z\pi$) bond overlaps of opposite phase, Ψ_+ and Ψ_- *above*